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Article

Effect of methanol concentration on oxygen reduction reaction activity of Pt/C catalysts

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ABSTRACT

The oxygen reduction reaction (ORR) activity of Pt/C catalysts was investigated in electrolytes of 0.5 mol/L H_2SO_4 containing varying concentrations of methanol in a half-cell. It was found that the ORR activity was improved notably in an electrolyte of 0.5 mol/L H_2SO_4 containing 0.1 mol/L CH_3OH as compared with that in 0.5 mol/L H_2SO_4, 0.5 mol/L H_2SO_4 containing 0.5 mol/L CH_3OH, or 0.5 mol/L H_2SO_4 containing 1.0 mol/L CH_3OH electrolytes. The same tendency for improved ORR activity was also apparent after commercial Nafion® NRE-212 membrane was hot-pressed onto the catalyst layers. The linear sweep voltammetry results indicate that the ORR activities of the Pt/C catalyst were almost identical in the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH solution before and after coated with the Nafion® membrane. Electrochemical impedance spectroscopy results demonstrated that the resistance of the Nafion® membrane is smaller in the electrolyte of 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH than in other electrolytes with oxygen gas feed. This exceptional property of the Nafion® membrane is worth investigating and can be applied in fuel cell stacks to improve the system performance.

1. Introduction

The direct methanol fuel cell (DMFC) is one of the most promising candidates for portable power sources. One of the current challenges for this industry is methanol crossover that leads to the poisoning of cathode catalysts and environmental pollution [1–3]. Therefore, the development of a methanol resistant membrane and methanol-tolerant catalysts is of great importance in developing DMFCs.

Extensive studies have been carried out to improve the activities of catalysts [4,5], develop methanol resistant membranes [6–9], and methanol-tolerant catalysts [10–13]. Pd-Pt nanodendrites were synthesized by reducing K_2PtCl_4 with L-ascorbic acid in the presence of uniform Pd nanocrystal seeds. On the basis of equivalent Pt mass for the ORR, these were two and a half times more active in an aqueous solution than state-of-the-art Pt/C catalysts. They were also five times more active than first-generation Pt-black catalysts because of the controlled morphology of Pt nanostructures [4,5]. Ren et al. [6] prepared organic silica with thiol group/Nafion® composite membranes by using a casting method that used various additives including $HS(CH_2)_3CH_3Si(OCH_3)_2(SH–)$, tetraethyl orthosilicate (TEOS), and $HS(CH_2)_3CH_3Si(OCH_3)_2$-TEOS (HS-TEOS) in Nafion® solutions. The 125 μm SH-TEOS/ Nafion® composite membranes showed an approximately 50% decrease of methanol crossover compared with that of commercial Nafion® 117 membrane. However, the proton conductivity of the membrane was slightly lowered. Core-shell PtM/C (M = Fe, Co, Ni, Pd, Cu, etc) catalysts are regarded as good methanol-tolerant catalysts because of their higher platinum surface area and unique alloy

structure [10–13].

The influence of methanol on catalyst activity and catalyst layers have been investigated by AC impedance [14–18]. Du et al. [16] reported that the half-cell was ideal for the Electrochemical Impedance Spectroscopy studies of DMFC electrodes as the system not only facilitates an accurate potential control but also reflects the actual mass transport process that occurs in practical DMFCs. The steady-state results confirmed that the presence of methanol at the cathode could lead to a significant poisoning effect on the ORR, especially when the DMFC operates at higher methanol concentrations and discharges at lower potentials. Affoune et al. [17] measured the conductivity and surface morphology of Nafion® 117 membranes in water and alcohol environments, where the conductivity was 0.1013, 0.0206, 0.0311, 0.0667, and 0.0912 S/cm for water, pure methanol, and methanol-H_2O solutions with CH_3OH/H_2O volume ratios of 75%–25%, 50%–50%, and 25%–75%, respectively. The proton conductivity decreased with increasing methanol content [17]. Aricò et al. [18] used a gas diffusion electrode that mounted into a Teflon holder containing a platinum ring current collector and having an oxygen gas feed (1 × 10^5 Pa, 200 cm³/min) as the working electrode. The oxygen reduction behaviors of the electrodes coated and uncoated by Nafion® film were characterized in solutions of 2.5 mol/L H_2SO_4 and 2.5 mol/L H_2SO_4 containing 0.5 mol/L CH_3OH electrolyte. The oxygen reduction process was more favorable at low current densities with the Nafion® coated electrode. The open circuit voltage was approximately 200 mV higher for this electrode than the analogous uncoated electrode. At current densities higher than 100 mA/cm², the activity of the prepared electrode surpasses that of the Nafion®coated electrode. These phenomena have been interpreted on the basis of the large oxygen solubility of the Nafion® electrolyte-electrode interface that causes a decrease of over-potential at low current density. Ohmic drop and mass transfer control significantly reduce the activity of Nafion®-coated electrodes at high currents. At potentials lower than those corresponding to Pt-oxide reduction, methanol is oxidized even in the cathodic polarization [18].

In this paper, carbon diffusion layers were coated with Pt/C catalysts (Johnson Matthey Company) of different Pt loadings and investigated in a 0.5 mol/L H_2SO_4 solution containing varying concentrations of methanol. Commercial membrane Nafion® NRE-212 was then hot-pressed onto the surface of the catalyst layers and the half-membrane electrode assembly (half-MEA) was investigated under identical conditions. Several notable results were obtained when Pt/C catalysts and the half-MEAs were tested in 0.5 mol/L H_2SO_4 solutions containing different concentrations of methanol.

2. Experimental

2.1. Preparation of gas diffusion layer

Toray carbon paper (TGP-H-030, Toray, Japan) was treated by a 6 wt% PTFE emulsion until the dry PTFE loading reached ca. 0.8 mg/cm². The slurry of carbon black Vulcan XC72R and PTFE (w/o = 1:1) was then brushed onto both sides of the PTFE-treated carbon paper until the carbon loading was approximately 1.5 g/cm². The gas diffusion layer was prepared after being treated at 340 °C for half an hour under nitrogen flow.

2.2. Fabrication of working electrodes

Pt/C (20 wt% HiSPEC™ 3000, Johnson Matthey) and Pt/C (50 wt% HiSPEC™ 8000, Johnson Matthey) catalyst inks were prepared with a mass ratio of 10:90 or 15:85 for dry Nafion®/catalyst, respectively. Cutting the gas diffusion layer into discs of Ø = 13 (s = 1.3273 cm²), the catalyst ink was then dropped onto one side of the disc repeatedly. After the catalyst
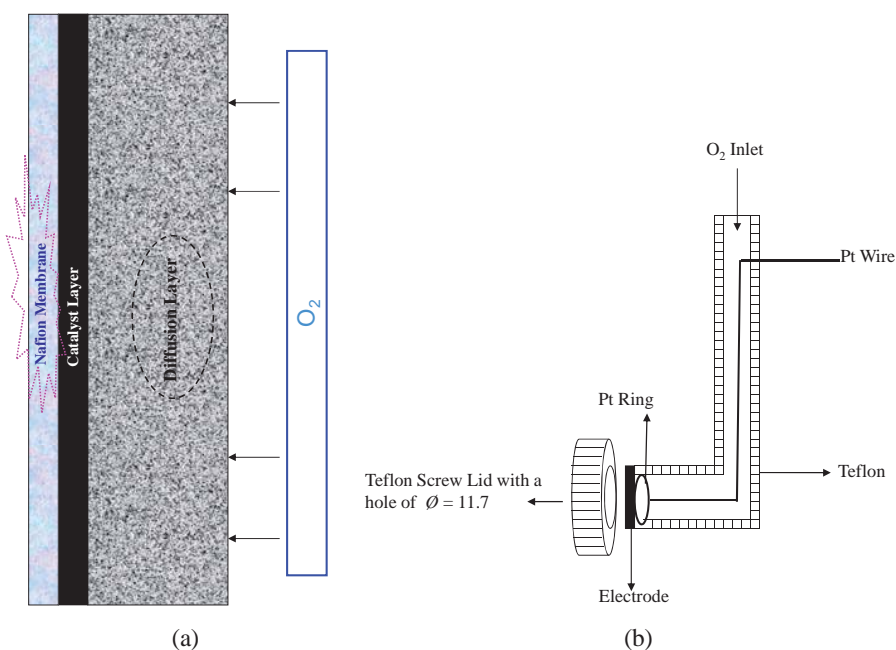

Fig. 1. Schematic structure of electrode (a) and configuration of working electrode (b).

ink dried, the electrodes were treated in an oven at 80 °C for half an hour. Two parallel catalyst electrodes were fabricated and tested for each catalyst.

2.3. Electrochemical measurements

The ORR activity of 20 wt% Pt/C catalysts was tested in the electrolytes of 0.5 mol/L H_2SO_4 containing different concentrations of methanol. After that, the electrode was taken out of the electrolyte and rinsed with high purity of water, then dried in an 80 °C oven. Subsequently Nafion® perfluorinated resin solution (5 wt%) was dropped onto the top of the catalyst layer to form a thin film, then two layers of pre-treated commercial Nafion® membrane NRE-212 (Aldrich, Item# 676470) were hot-pressed onto the catalyst layer one by one at 130 °C, which is denoted as half-MEA. The above mentioned tests were performed again. At the same time, a new untested electrode was hot-pressed with Nafion® NRE-212 membrane and subsequently investigated. For 50 wt% Pt/C (HiSPEC™ 8000, Johnson Matthey) catalysts, both electrodes were hot-pressed with two layers of Nafion® NRE-212 membrane before testing.

The configuration of the half-MEA is shown in Fig. 1 (a). The electrode or half-MEA was mounted onto a Teflon skeleton with the catalyst layer or Nafion® membrane exposed to the electrolyte. Oxygen was introduced from the back of the catalyst layer as shown in Fig. 1 (b), which is similar to that described in reference [18]. All measurements were carried out in a three-electrode cell. A Pt slice was used as the counter electrode, and Ag/AgCl(s) electrode was used as the reference electrode. The potentials mentioned below were recorded against Ag/AgCl(s) unless noted. Oxygen was introduced for more than 10 min before linear sweep voltammetry (LSV) tests or electrochemical impedance spectroscopy (EIS) measurements. After changing the electrolyte, oxygen was stopped for half an hour to ensure the replaced electrolyte efficiently gets access to the catalyst layer. The electrodes were not rinsed if they were placed in more concentrated electrolyte; however, they were rinsed with high purity de-ionized water when placed in a diluted electrolyte.

3. Results and discussion

The compositions of the electrodes or half-MEAs of 20 wt% Pt/C and 50 wt% Pt/C catalysts are listed in Table 1.

3.1. Influence of methanol concentration on ORR activity
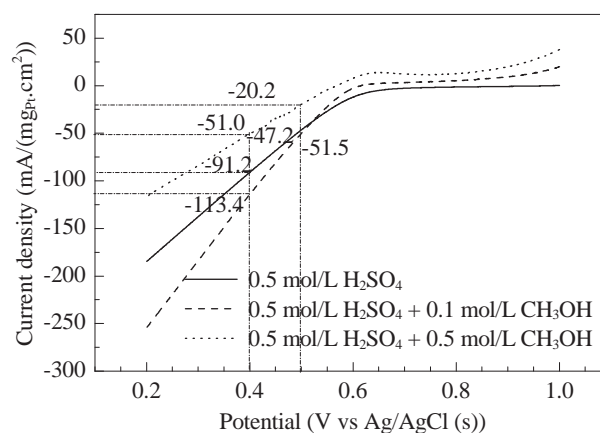
The ORR activities of 20 wt% Pt/C catalysts in different

Table 1
The parameters of electrodes or half-MEAs.

Item	Catalyst mass (mg)	5 wt% Nafion® solution	Pt loading (mg_{Pt}/cm^2)	Nafion® loading (mg/cm^2)
20 wt% Pt/C (Johnson Matthey)	10.4 wt%	dry Nafion®	0.47	24.5
			0.62	N/A
50 wt% Pt/C (Johnson Matthey)	15.0 wt%	dry Nafion®	4.13	25.5
			4.74	26.8

Fig. 2. LSV curves of 20 wt% Pt/C (Johnson Matthey) in different electrolyte at room temperature. Potential scan range of 1.1–0.2 V vs Ag/AgCl (s), scan rate of 5 mV/s, and oxygen flow rate of 50 ml/min.

electrolytes are shown in Fig. 2. In the potential range from 1.1–0.7 V, the current density is noted to be influenced by methanol concentration. The curve at ~0.64 V can be assigned as the combination of methanol and oxygen, where the methanol creates an oxidation current and the oxygen causes a reduction current. In the 0.5 mol/L H_2SO_4 electrolyte, there is no oxidation current of methanol, and the onset potential of oxygen reduction is approximately 0.62 V. In 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH electrolyte, the oxidation current of methanol is almost offset by the reduction current of the oxygen. However, if the electrolyte contains more concentrated methanol, the oxidation current of methanol is higher than the reduction current of oxygen.
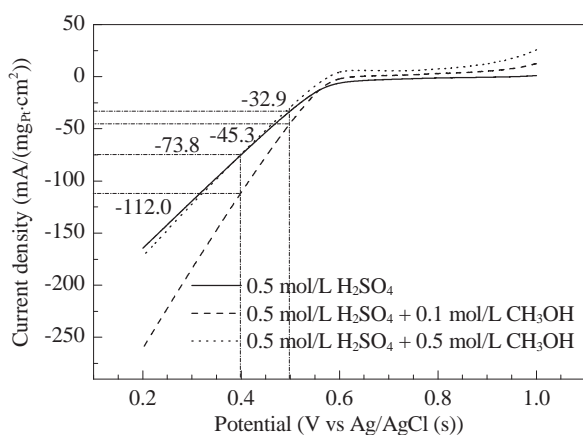
At a potential of 0.5 V, the ORR activity is −47.2 mA/($mg_{Pt}.cm^2$) in 0.5 mol/L H_2SO_4. It is −51.5 mA/($mg_{Pt}.cm^2$) in 0.5 H_2SO_4 + 0.1 mol/L CH_3OH and −20.2 mA/($mg_{Pt}.cm^2$) in 0.5 H_2SO_4 + 0.5 mol/L CH_3OH. At a potential of 0.4 V, the ORR activity was enhanced from −91.2 mA/($mg_{Pt}.cm^2$) to −113.4 mA/($mg_{Pt}.cm^2$) when replacing the 0.5 mol/L H_2SO_4 solution by 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH. However, the activity decreased to −51.0 mA/($mg_{Pt}.cm^2$) when replaced by 0.5 mol/L H_2SO_4 + 0.5 mol/L CH_3OH. The effect of methanol concentration on the ORR activity is highly noticeable. Previously, it had only been considered that methanol causes poisoning of the cathode Pt/C catalyst, so the study of methanol-tolerant catalysts was determined as one of the most important aspects in the development of DMFCs [10–13]. However, from the results above, the ORR activity of Pt/C catalysts has been shown to improve significantly in a 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH electrolyte. If the ORR activity of Pt/C catalysts in a 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH solution can be used in DMFC stacks by specialized design, system performance can be improved.

To gain more practical data, the half-MEA with two layers of pre-treated Nafion® NRE-212 membrane hot-pressed on the catalyst layer were investigated. The LSV curves of the half-MEA of 20 wt% Pt/C catalyst in 0.5 mol/L H_2SO_4, 0.5 mol/L H_2SO_4 + 0.1 CH_3OH, and 0.5 mol/L H_2SO_4 + 0.5 CH_3OH solutions are shown in Fig. 3. As the Nafion® membrane may have covered some active sites of the catalyst, the ORR activity of the

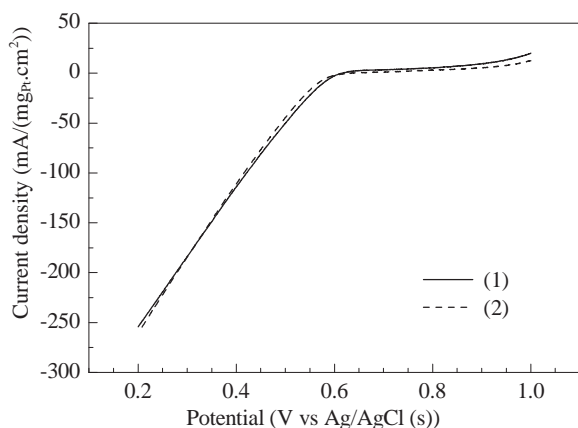**Fig. 3.** LSV curves of 20 wt% Pt/C (Johnson Matthey) after coated with two layers of commercial Nafion® membrane NRE-212. Potential scan range of 1.1–0.2 V vs Ag/AgCl (s), scan rate of 5 mV/s and oxygen flow rate of 25 ml/min at room temperature.

catalyst in 0.5 mol/L H_2SO_4 solution decreased from –91.2 to –75.8 mA/($mg_{Pt}.cm^2$). In the 0.5 mol/L H_2SO_4 + 0.5 CH_3OH solution, the Nafion® membrane can prevent the Pt/C catalyst from being exposed to methanol directly, thus improving the ORR activity. The behavior is similar to that recorded in the absence of methanol at potentials lower than 0.5 V. As in the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH solution, the catalyst activity was barely affected by the Nafion® membrane, because it was almost identical to that of the uncoated electrode, as shown in Fig. 4. It appears that the Nafion® membrane did not cover the active sites and the methanol did not lead to poisoning of the catalyst in the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH electrolyte. The ORR activity was significantly enhanced compared with that in the 0.5 mol/L H_2SO_4 solution. This could be due to more open micro-channels for proton transfer in the Nafion® membrane other than the swelling in the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH electrolyte, which could subsequently lead to smaller resistance of the Nafion® membrane. This tendency may also be because of the promotion effect of methanol in the oxygen reduction reaction in the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH electrolyte, which could lead to reduced charge transfer resistance.
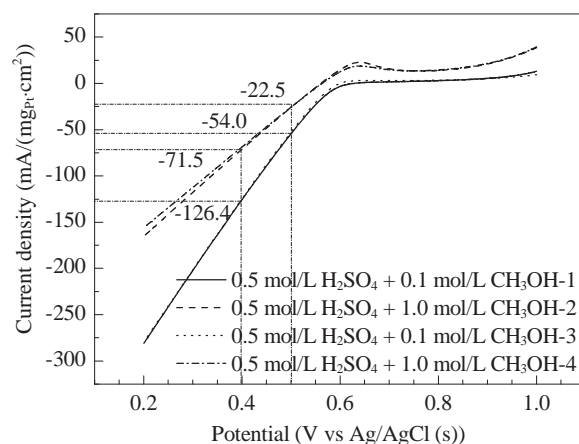
Usually in a single cell or stack, 1.0 mol/L or higher concentrations of CH_3OH solution are introduced as fuel. At the potential of 0.5 V, the ORR activity of the half-MEA of 20 wt% Pt/C catalyst can increase from –22.5 to –54.0 mA/($mg_{Pt}.cm^2$) after the electrode is transferred from the 0.5 mol/L H_2SO_4 + 1.0 mol/L CH_3OH to the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH electrolyte. At the potential of 0.4 V, the ORR activity can increase from –71.5 to –126.4 mA/($mg_{Pt}.cm^2$). Furthermore, the ORR activity of the Pt/C catalyst in the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH solution can be recovered after being tested in the 0.5 mol/L H_2SO_4 + 1.0 mol/L CH_3OH solution, and even enhanced slightly after several cycles. The LSV curves are shown in Fig. 5.

To further support practical stack application, 50 wt% Pt/C catalysts with a catalyst loading of ca. 4.0 mg_{Pt}/cm^2 were investigated. The ORR activities of half-MEA of 50 wt% Pt/C catalysts in a 0.5 mol/L H_2SO_4 solution containing different methanol concentrations are shown in Fig. 6. A similar trend was obtained for 50 wt% Pt/C catalysts. The ORR activities of the catalysts were almost identical in 0.5 mol/L H_2SO_4, 0.5 mol/L H_2SO_4 + 0.5 mol/L CH_3OH, and 0.5 mol/L H_2SO_4 + 1.0 mol/L CH_3OH solutions at potentials of lower than 0.5 V, but was enhanced in 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH. The most noticeable differences in electrolytes containing varying concentrations of methanol were observed at potentials higher than 0.6 V. More serious methanol crossover was observed in higher concentrations of methanol solutions that produced a larger methanol oxidization current. However, at potentials lower than 0.5 V, they demonstrated similar activities, except for that in the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH solution.

From Figs. 3 and 5, the methanol crossover affects the LSV curves at potentials higher than ca. 0.5 V, but has little influence at lower potentials. This implies that the oxygen reduction reaction is dominant at lower potentials, with methanol only contributing a very slight oxidation current or none at all. The onset potentials shifted cathodically in 0.5 mol/L H_2SO_4 + 0.5 mol/L CH_3OH or 0.5 mol/L H_2SO_4 + 1.0 mol/L CH_3OH solutions as the active sites of the Pt/C catalysts were occupied by CO-like intermediates from the methanol oxidation reaction at

Fig. 4. Comparison of LSV curves of 20 wt% Pt/C (Johnson Matthey) before (1) and after coated with Nafion® membrane NRE-212 (2).

Fig. 5. LSV curves of 20 wt% Pt/C (Johnson Matthey) coated with Nafion® membrane NRE-212 were tested in different electrolytes at room temperature. Numbers 1, 2, 3, and 4 were used to denote the testing sample sequence.
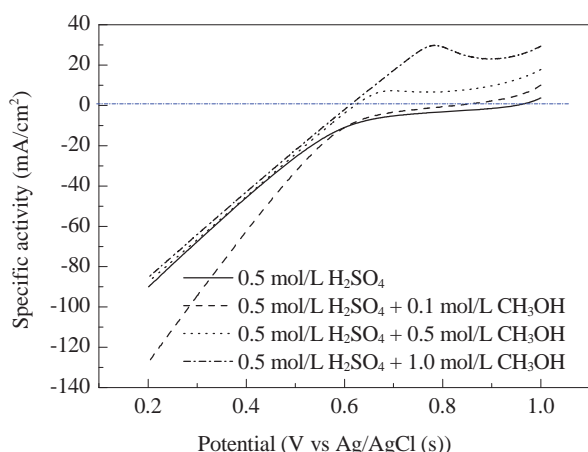
Fig. 6. Comparison of linear sweep voltammetry of 50 wt% Pt/C (Johnson Matthey) coated with Nafion® membrane NRE-212 in different electrolytes at room temperature.

higher potentials, leading to the poisoning of Pt/C catalysts. However, it is not clear why small amounts of methanol in the electrolyte do not lead to poisoning of Pt/C catalysts, rather than improving the ORR activity.

During preparation of the catalyst ink, the catalyst particles were partly covered by a Nafion® thin film, so the catalysts utilization is usually less than 20%. The methanol solution can open or enlarge the proton transfer micro-channels of the Nafion® membrane, which would lead to methanol crossover and membrane swelling. However, more open micro-channels can lead to higher proton transfer capacity, and more oxygen can get access to active sites of Pt/C catalysts. More active sites of the Pt/C catalyst can be exposed to oxygen and/or proton thus the three-phase interfaces can be more easily maintained, which is defined as a promotional effect of methanol. If the methanol concentration is too high, the methanol crossover and membrane swelling will be more serious, thus the negative effects of methanol will dominate. However, if the methanol concentration is within acceptable limits, methanol can maximize the capacity of proton transfer, and more oxygen can access more active sites, thus promoting the positive effects of

methanol, such as in the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH solution. Affoune et al. [17] measured the proton conductivity of Nafion® 117 membrane in a CH_3OH/H_2O electrolyte with volume ratios of 75%–25%, 50%–50%, and 25%–75%. They drew the conclusion that proton conductivity decreased with increased methanol content. However, the most dilute electrolyte used in their paper was of 25% methanol-75% H_2O, with a molar concentration of ca. 6.0 mol/L, which is too concentrated as a direct feed fuel for DMFCs. Thus their conclusion is not applicable in this study.

3.2. Influence of methanol concentration on AC impedance

Electrochemical impedance spectroscopy can be a helpful technique to probe reaction processes [14–18]. For identical system configurations, the difference in impedance spectroscopes can reflect the differences in the EC or half-MEA. Half-MEAs of 20 wt% Pt/C and 50wt% Pt/C catalysts in a 0.5 mol/L H_2SO_4 solution containing different concentrations of methanol were measured at different potentials in a frequency range from 100 kHz–10 mHz.

Nyquist plots are demonstrated in Fig. 7 for half-MEAs of 20 wt% Pt/C and 50 wt% Pt/C catalysts in 0.5 mol/L H_2SO_4 electrolytes containing different contents of methanol. Electrolyte resistance was 3.81 Ω for the half-MEA of 20 wt% Pt/C catalyst in 0.5 mol/L H_2SO_4, 2.49 Ω for the solution of 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH, and 3.88 Ω for the 0.5 mol/L H_2SO_4 + 0.5 mol/L CH_3OH electrolyte. The resistances were slightly larger in 0.5 mol/L H_2SO_4 + 0.5 mol/L CH_3OH than in 0.5 mol/L H_2SO_4, but were much smaller in 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH. The same tendency was observed for the half-MEA of 50 wt% Pt/C catalysts. The resistances were 3.80 Ω for the half-MEA of 50 wt% Pt/C catalyst in 0.5 mol/L H_2SO_4, 2.63 Ω for the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH solution, 3.96 Ω for 0.5 mol/L H_2SO_4 + 0.5 mol/L CH_3OH, and 4.12 Ω in 0.5 mol/L H_2SO_4 + 1.0 mol/L CH_3OH. The major difference between the two half-MEAs lies in the charge transfer resistance. The half-MEA of 50 wt% Pt/C catalyst with high platinum loading (more than 4 mg_{Pt}/cm^2) demonstrated a smaller charge transfer resistance,
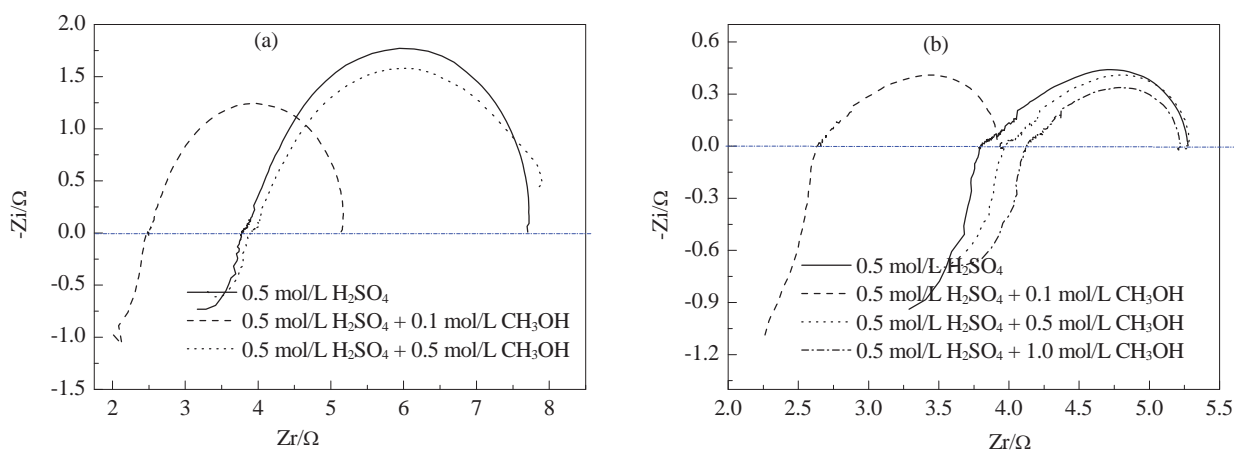
Fig. 7. Nyquist plots of 20 wt% Pt/C (a) and 50 wt% Pt/C (b) coated with Nafion® membrane NRE-212 at potential of 500 mV with potential step of 10 mV and AC sine wave amplitude of 10 mV between 100 kHz and 10 mHz, in 0.5 mol/L H_2SO_4 containing varying concentrations of CH_3OH at room temperature.

that is why high Pt loading is needed for DMFCs. As more concentrated methanol in the electrolyte was applied, smaller charge transfer resistances were observed. This indicates that in some cases, methanol can facilitate the charge transfer process in the oxygen reduction reaction. This is consistent with the reports by Aricò et al. [18].

The EIS results were found to correlate with the ORR activity results. As mentioned previously, more micro-channels of the Nafion® membrane were enlarged because of the oxygen gas present in the 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH solution, thus leading to the smaller resistances and improved ORR activity. This special property of Nafion® membranes can be used in designing a stack that will improve the performance of fuel cells. Pt/C catalysts (20 wt%) from E-TEK company, in-house Pt/C and PtCo/C catalysts were also measured and the same trends were obtained. The improved ORR activity of the Pt/C catalysts in 0.5 mol/L H_2SO_4 + 0.1 mol/L CH_3OH solution has been noted in all the testing data. Further research will be carried out to investigate the theory behind these results.

4. Conclusions

Both catalysts of 20 wt% Pt/C and 50 wt% Pt/C (Johnson Matthey) showed much better oxygen reduction reaction activities in electrolytes in 0.5 mol/L H_2SO_4 solutions containing 0.1 mol/L CH_3OH. This was due to reduced electrolyte resistances. The charge transfer resistances can also be reduced in more concentrated methanol solutions by increasing the Pt loading of the electrode. High Pt loading at the electrode can be adopted for practical use and 0.1 mol/L CH_3OH can be fed to a direct methanol fuel cell. This can increase the efficiency of the overall system and reduce environmental pollution for portable power devices.

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Graphical Abstract

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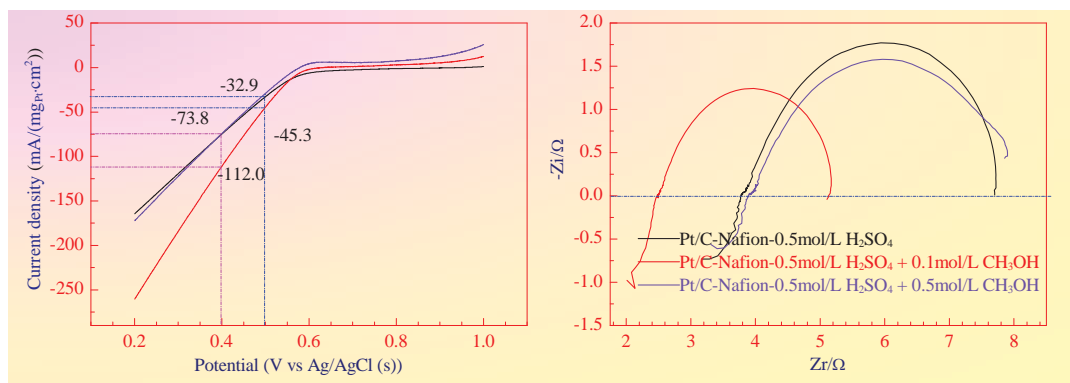
The ORR activity of 20 wt% Pt/C catalyst was enhanced notably due to a smaller resistance of Nafion membrane in the electrolyte of 0.5 mol/L H_2SO_4 containing 0.1 mol/L methanol with oxygen gas feed.

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甲醇浓度对**Pt/C**催化剂氧还原活性的影响

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摘要: 采用半池考察了Pt/C催化剂在含不同浓度甲醇的0.5 mol/L硫酸中的氧还原活性(ORR). 研究发现, 当甲醇浓度为0.1 mol/L时, Pt/C催化剂的ORR活性最高, 在催化层上热压商品Nafion NRE-212膜后也出现同样趋势. 线性扫描伏安曲线显示, 压膜前后的Pt/C 催化剂的ORR活性在含0.1 mol/L甲醇的0.5 mol/L硫酸中几乎没有变化. 电化学阻抗谱结果表明, 在该溶液中, Nafion膜的电阻比在其它电解液中低, 这可能是导致Pt/C催化剂ORR活性提高的主要原因. 有必要关注Nafion膜的这一异常性质并通过特殊设计后用于电池堆, 以提高燃料电池性能.

关键词: 铂; 炭; 甲醇渗透; 氧还原; 燃料电池